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Effects of Coordination Environment on the Zr-F Symmetric Stretching Frequency of Fluorozirconate Glasses, Crystals, and Melts

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A treatment based on Badger's rule is used to estimate symmetric stretching frequencies, v_s , of various ZrF_n groups in the presence of divalent and monovalent counterions. New vibrational spectra of $MgZrF_6$, Ba_2ZrF_8 , and $\beta\text{-BaZr}_2F_{10}$ are presented and incorporated into the method. The factors affecting v_s are outlined and discussed in detail. Compilations of estimated frequencies are applied to the interpretation of local structure around Zr ions in binary barium fluorozirconate glasses and in fluorozirconate melts containing lithium and sodium ions. It is concluded that the presence of 8-coordinate Zr in some barium fluorozirconate glasses is not inconsistent with the results of Raman spectroscopy.

I. INTRODUCTION

The possible technological applications and the uncommon atomic structures of fluorozirconate glasses have provoked a considerable research effort in recent years. The nature of the fluoride-ion arrangements around zirconium has been much debated but is still not known with certainty. Vibrational spectroscopy, especially Raman spectroscopy, has proved to be a sensitive indicator of the immediate environment of zirconium. In particular, the totally symmetric stretching frequency of the fluorides that are bonded to only one zirconium (the nonbridging, or terminal, fluorides) has been used as a probe of the zirconium surroundings. Several aspects of the nearby solid-state environment can influence this symmetric stretch frequency, otherwise known as v_s , but there has been no systematic attempt to categorize or to quantify these influences. In order to minimize complications (such as effects from several different components in glasses), we will focus on Raman spectra of fluorozirconate crystals of known structure and compare them with spectra of binary barium fluorozirconate glasses. This study outlines the effects on v_s due to different environmental factors and predicts approximate frequencies expected for various types of F-about-Zr coordinations.

II. EXPERIMENTAL PROCEDURE

III. RESULTS

{Raman spectra of MgZrF₆, Ba₂ZrF₈, and β-BaZr₂F₁₀ -- Fig. 1, Fig. 2, Fig. 3.}

IV. METHOD FOR ESTIMATING FREQUENCIES

The five factors influencing the ν_s frequency are: 1) the radius of the countercation (e.g., Ba²⁺), 2) the coordination number (CN) of the counterocation, 3) the degree of bridging between Zr ions, 4) the CN of Zr, and 5) the charge on the countercation. The effects of these conditions will be discussed individually after the development of some empirical relationships between force constants, the nature of the countercation, and bond strengths.

A. EFFECT OF COUNTERCATION RADIUS ON FORCE CONSTANT

Badger [Ba35] reported an empirically derived equation relating force constants of diatomic molecules to internuclear separation:

$$k^{-\frac{1}{3}} = a_{ij} \cdot r_e - b_{ij}, \quad (1)$$

where k is the force constant, r_e is the internuclear distance, and a_{ij} and b_{ij} are constants for all diatomic molecules with one element from the i th row and one element from the j th row of the periodic table. The value of a_{ij} , the slope of the equation, is not very variable. In fact, since plots of $k^{-\frac{1}{3}}$ vs. r_e give straight, almost parallel lines for many different types of diatomics, a_{ij} was originally described [Ba34] as a universal constant over all molecules. Badger's equation has proved to be remarkably accurate in its predictions. Waser and Pauling [Wa50] showed that it can be applied to the solid state.

As stated above, the variable r_e in the Badger rule refers to internuclear separation. A more general measurement is needed, for two reasons: 1) there is not a plethora of crystal data available for fluorozirconates, and 2) we wish to extend the approach to estimate frequencies of structures which are not known to occur in crystals. The more general variable r_M , the radius of the countercation, shows a definite correspondence with r_e for the Zr-T (T = terminal fluoride) separation, as shown in Fig. 4 for some sets of isostructural divalent and isostructural trivalent fluorozirconate crystals. (All ionic radii used in this paper are taken from or calculated from data reported in [Sh76].) Eq. 1 may therefore be written as

$$k_T^{-\frac{1}{3}} = A \cdot r_M + B, \quad (2)$$

where k_T is the force constant associated with the terminal-fluoride stretch, and A and B are constants. The slope, A , would be expected to be relatively constant for similar structures.

An approximation to k_T can be calculated directly from ν_s using the relation

$$\nu_s = \frac{1}{2\pi c} \sqrt{\frac{k_T}{m_F}}, \quad (3)$$



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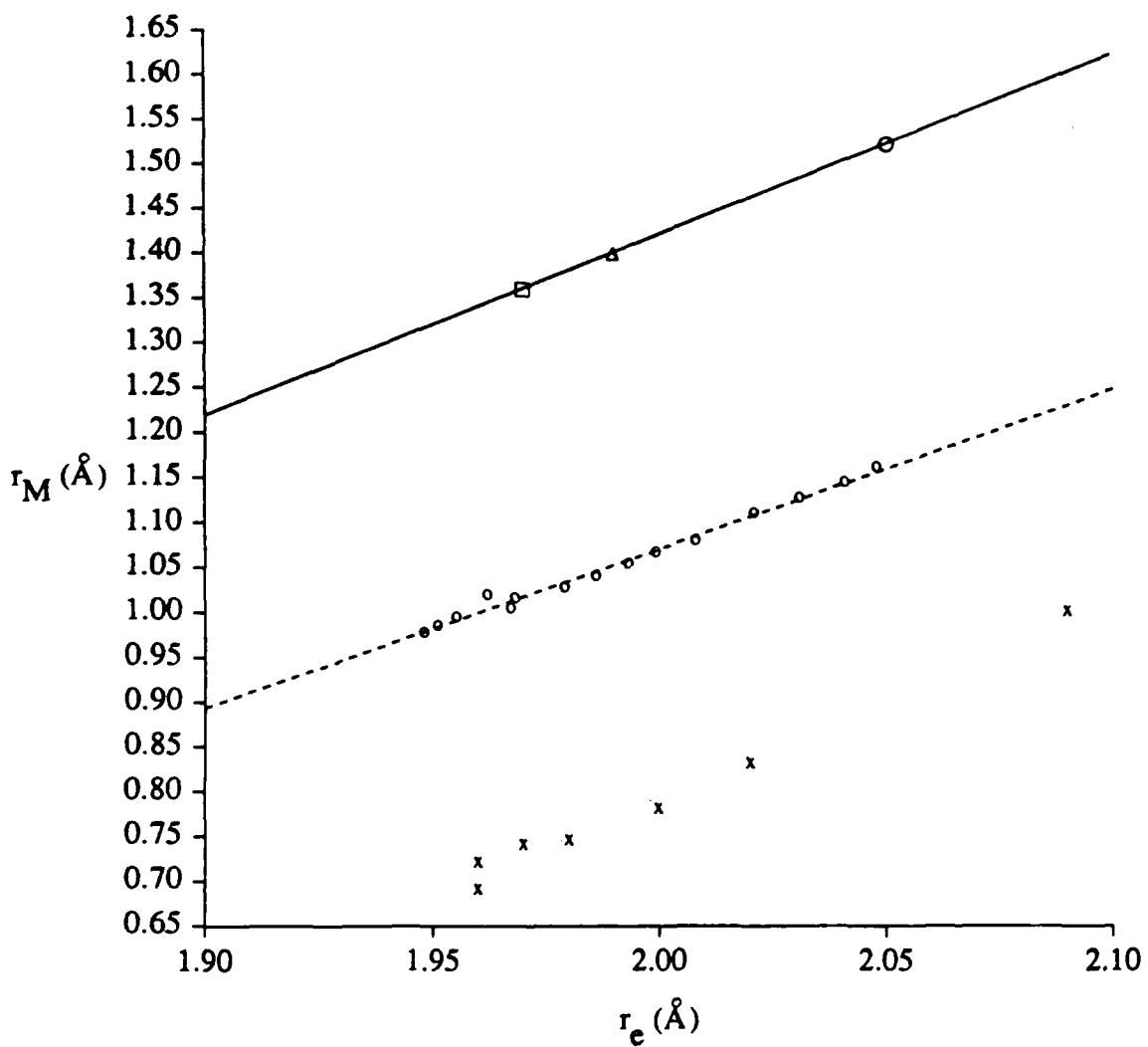


Fig. 4. Plot of countercation radius vs. Zr-T internuclear separation for some isostructural fluorozirconate crystals. For the solid line, the circle represents β -BaZrF₆, the triangle is PbZrF₆, and the square is α -SrZrF₆ (r_e values from [La74]). The dashed line refers to LnZrF₇ compounds, where Ln is an 8-coordinate lanthanide ion (r_e values calculated from data in [Po72] and [Po73]). The dotted line contains points for cubic MZrF₆ compounds, where M is a 6-coordinate divalent ion (r_e values calculated from data in [Po70] and [Ma83]).

which is strictly applicable only for the case of harmonic motion in diatomic molecules. In Eq. 4, v_s is in wavenumbers, c is the speed of light in cm/s, k_T is in dyne/cm, and m_F is the mass of a fluorine atom. It is assumed that there is no motion of Zr atoms during the symmetric stretching vibration.

Table I. Data for isostructural fluorozirconate crystals containing divalent counterions. The v_s values are from [Ka83].

	$v_s(\text{cm}^{-1})$	$k_T(\text{mdyne}/\text{\AA})$	$r_M(\text{\AA})$
$\alpha\text{-SrZrF}_6$	578	3.74	1.36
PbZrF_6	567	3.60	1.40
$\beta\text{-BaZrF}_6$	562	3.54	1.52

The structure of the crystals in Table I can be written in a "shorthand" manner as $M^{II}\{10\}ZrT_4E_4$, indicating that the counterion is divalent with a CN of 10 and that the Zr is 8-coordinate, with 4 terminal fluorides and 4 edge (doubly bridging) fluorides. Using the information shown in Table I, the effects of different counterions on k_T can be written as

$$k_T^{-\frac{1}{3}} = 0.065914 \cdot r_M + 0.55674 \quad (4)$$

for the $M^{II}\{10\}ZrT_4E_4$ type of structure. An excess number of digits is being retained in the coefficients to minimize truncation error in future steps. In analogy with the Badger rule, the slope of this equation should be nearly the same for other isostructural crystals differing only in the identity of the counterion. This is seen to be the case for the alkali fluorozirconate crystals listed in Table II.

Table II. Data for isostructural fluorozirconate crystals containing monovalent counterions. The v_s values for the Rb and Cs compounds are from [Fo76] and [De67], respectively.

	$v_s(\text{cm}^{-1})$	$k_T(\text{mdyne}/\text{\AA})$	$r_M(\text{\AA})$
$\beta\text{-Rb}_2\text{ZrF}_6$	589	3.89	1.72
$\beta\text{-Cs}_2\text{ZrF}_6$	576	3.72	1.88

The equation is

$$k_T^{-\frac{1}{3}} = 0.059578 \cdot r_M + 0.53344 \quad (5)$$

for the $(M^I\{12\})_2\text{ZrT}_6$ type of structure. The coordination number of M^I is 9+3, and 12 is an acceptable description [Ho39, Si52].

Since the v_s and the r_M values for $MgZrF_6$ are known (Section III), it would be possible to estimate from an appropriate equation the frequency expected for an isostructural crystal containing Ba rather than Mg, even though such a crystal does not exist. If an average of the slopes of Eqs. 4 and 5 is used for the new equation, we obtain

$$k_T^{-\frac{1}{3}} = 0.062746 \cdot r_M + 0.53898 \quad (6)$$

for the $M^{II}\{6\}ZrT_6$ structure type (r_M for 6-coordinate Mg^{2+} is 0.720 \AA). This yields a value of 606 cm^{-1} for the frequency of the hypothetical 6-coordinate Ba crystal, whose r_M value is 1.35 \AA . (The information from Eqs. 4-6 is graphed in Fig. 5.)

However, the Ba CN in glasses is almost certainly higher than 6. The results of Shafer and Perry [Sh79] indicate a value of 12 (or somewhat lower [Ph88]), and the most common Ba CN in the known barium fluorozirconate crystals is 11 [Ph88]. For comparison with glass spectra, it will therefore be necessary to determine the frequency for a Ba crystal with a higher Ba CN.

B. EFFECT OF COUNTERCATION COORDINATION NUMBER

Eqs. 4-6 apply to the case of substituting countercations of different sizes into isostructural crystals. The effect on v_s of changing the coordination number of a given countercation is a separate problem. The force constant expected for a hypothetical Li fluorozirconate crystal isostructural with the compounds listed in Table II (i.e., containing 12-coordinate Li) can be calculated from Eq. 5.

Table III. Data for lithium fluorozirconate crystals containing lithium with different coordination numbers. The v_s value for the compound with 6-coordinate Li is from [To73b], and the r_M value for 12-coordinate Li is from an exponential fit of data found in [Sh76].

	Li CN	$v_s(\text{cm}^{-1})$	$k_T(\text{mdyne}/\text{\AA})$	$r_M(\text{\AA})$
Li_2ZrF_6	12	(612)	(4.20)	(1.45)
Li_2ZrF_6	6	585	3.84	0.76

When the data for the crystal with 12-coordinate Li are compared with the information for a crystal containing 6-coordinate Li, as in Table III, the following equation for $(Li\{CN\})_2ZrT_6$ results:

$$k_T^{-\frac{1}{3}} = -0.027513 \cdot r_M + 0.65972 . \quad (7)$$

This equation shows the effects of changing the countercation CN, which can be converted to r_M using [Sh76]. Eq. 8 may be adapted to the case of $Ba\{CN\}ZrT_6$ by using the same slope and calculating a new intercept. This yields

$$k_T^{-\frac{1}{3}} = -0.027513 \cdot r_M + 0.66083 . \quad (8)$$

This means that the $BaZrT_6$ crystal with a Ba CN of 12 ($r_M = 1.61 \text{ \AA}$) would exhibit a v_s of

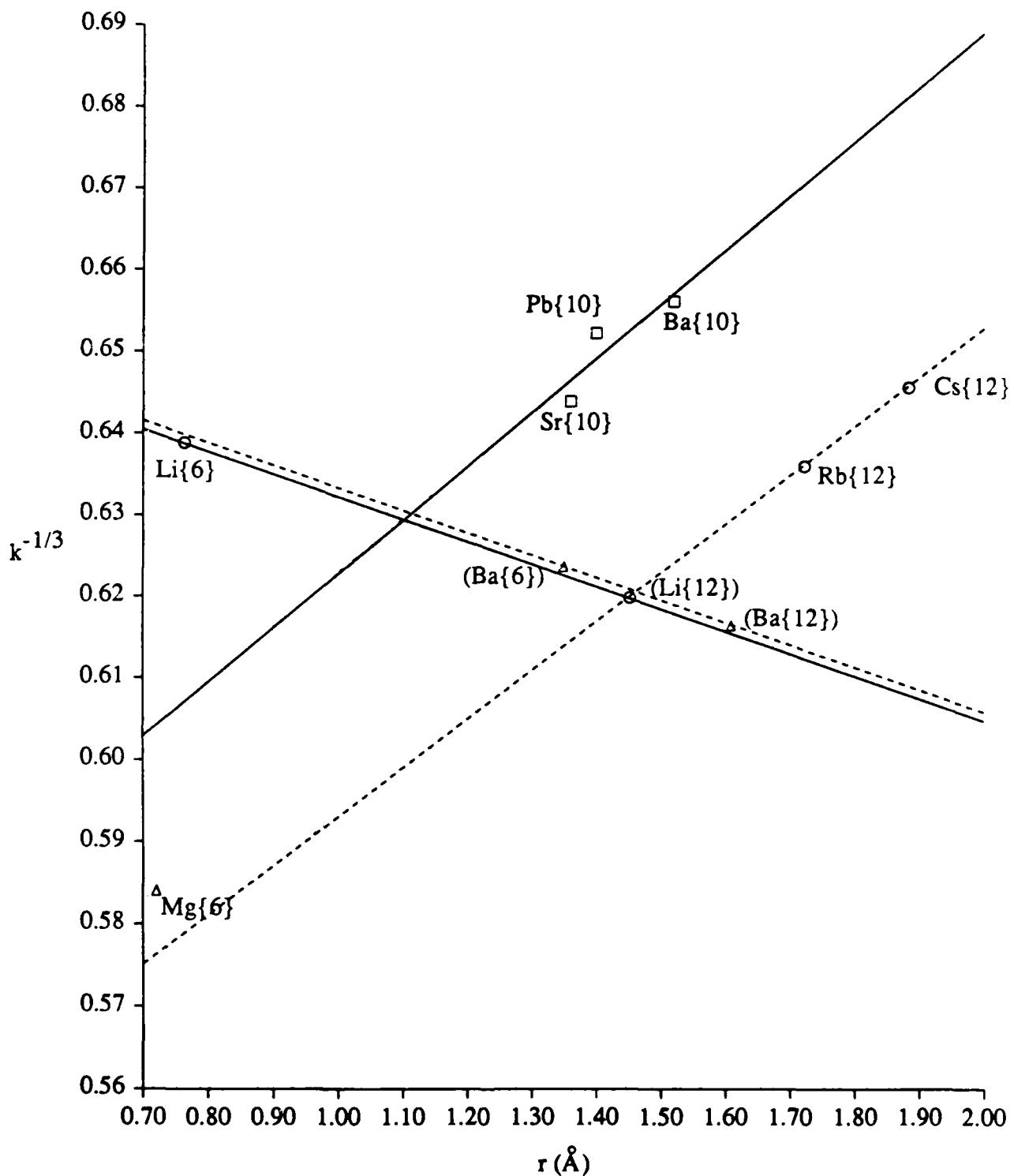


Fig. 5. The lines with positive slope are plots of $k^{-\frac{1}{3}}$ vs. counter cation radius for different sets of isostructural fluorozirconate crystals. Following the notation used in the text, the solid line refers to $M^{II}\{10\}ZrT_4E_4$, the dashed line to $(M^I\{12\})_2ZrT_6$, and the dotted line to $M^{II}\{6\}ZrT_6$. The lines with negative slope are plots of $\log k_T$ vs. counter cation CN (converted to radius using Ref. [Sh76]). The solid line refers to $(Li\{CN\})_2ZrT_6$ and the dashed line to $Ba\{CN\}ZrT_6$. The parentheses indicate calculated values.

about 617 cm^{-1} . Fig. 5 shows Eqs. 4-8 graphically.

This calculated v_s of 617 cm^{-1} may be compared with the results from Raman studies of a series of $\text{BaM}^{\text{IV}}\text{T}_6$ compounds containing 12-coordinate Ba.

Table IV. Data for $\text{BaM}^{\text{IV}}\text{T}_6$ crystals containing barium in 12-coordination. The $r_{\text{M(IV)}}$ values here refer to the central cation rather than the countercation.

	$v_s(\text{cm}^{-1})$	$k_T(\text{mdyne}/\text{\AA})$	$r_{\text{M(IV)}}C(\text{\AA})$
BaSiT_6	675.4	5.113	0.400
BaGeT_6	640.0	4.591	0.530
BaTiT_6	626.2	4.395	0.605

Table IV is taken from Ref. [Br77]. The v_s value for BaSnF_6 was not included because there is disagreement as to whether it is isostructural with the three compounds listed [Ref]. The original form of the Badger rule (Eq. 1) would be appropriate for the calculation of v_s for an isostructural BaZrT_6 crystal, but $r_{\text{M(IV)}}$ (where M(IV) refers to the central cation) will be used rather than r_e because there are no consistent r_e data for all three substances. The equation is

$$k_T^{-\frac{1}{3}} = 0.14829 \cdot r_{\text{M(IV)}} + 0.52166. \quad (9)$$

This leads to a value of 600 cm^{-1} for the hypothetical isostructural BaZrT_6 crystal ($r_{\text{M(IV)}} = 0.72 \text{ \AA}$). Both of the methods used for calculating the v_s of this crystal are necessarily in error to some degree. Since it is not known which value is "better," we will use the average of the two, 608 cm^{-1} in subsequent calculations.

C. RELATION BETWEEN FORCE CONSTANT AND BOND STRENGTH

The concept of bond strength, or bond valence, in inorganic compounds was first described by Pauling [Pa29]. If Z is the charge on a cation and CN is its coordination number, then the average bond strength, s, is given by

$$s = \frac{Z}{CN}. \quad (10)$$

In other words, the sum of the bond strengths around a cation is equal to the charge on the cation. Brown and Altermatt [Br85] devised an empirical relation between bond strength and r_e :

$$s = e^{(1.846 - r_e)/0.37}. \quad (11)$$

The above equation contains constants specific to the case of Zr bonded to F. Eqs. 1 and 11 may be combined to yield

$$k_T^{-\frac{1}{3}} = C \cdot \ln s + D. \quad (12)$$

The terminal bond strength for a F-about-Zr structure may be obtained by assuming that the bridging bond strength is a certain fraction of the terminal bond strength. For the barium fluorozirconate crystals known to contain bridging fluorides [La74, La78, La88], the s_C/s_T ratio

Table V. Zr-T bond strengths (s_T) for different types of ZrF_n polyhedra. Terminal and bridging (corner or edge) fluorides are denoted by T and B, respectively. The degree of bridging increases down a column in the direction from a to h.

$Zr\ CN \rightarrow$	6	7	8
a	ZrT_6 0.6667	ZrT_7 0.5714	ZrT_8 0.5000
b	ZrT_5B 0.7036	ZrT_6B 0.5984	ZrT_7B 0.5205
c	ZrT_4B_2 0.7449	ZrT_5B_2 0.6279	ZrT_6B_2 0.5427
d	ZrT_3B_3 0.7913	ZrT_4B_3 0.6606	ZrT_5B_3 0.5670
e		ZrT_3B_4 0.6969	ZrT_4B_4 0.5935
f		ZrT_2B_5 0.7373	ZrT_3B_5 0.6226
g			ZrT_2B_6 0.6547
h			$ZrTB_7$ 0.6903

is 0.763 and the average s_E/s_T ratio is 0.607, as calculated from Eq. 11. For generality, we will adopt an average s_B/s_T ratio of 0.685, where B signifies a bridging fluoride (corner or edge). Eq. 10, which is valid if all bonds around the central cation are of the same type, can be rewritten as

$$n_T s_T + n_B s_B = Z \quad (13)$$

when there are different types of bonds around the cation. In Eq. 13, n_T and n_B are respectively the numbers of terminal fluorides and bridging fluorides per Zr, and $n_T + n_B = CN$. The values of s_T and s_B for the different F-about-Zr structures shown in Table V were obtained by substituting $s_B = 0.685s_T$ and $Z = 4$ into Eq. 13.

The values of v_s from Table V will now be used to predict frequencies for various ZrF_n polyhedra as a function of the Zr CN and of the degree of bridging around Zr. For the compound Ba_2ZrF_8 , which is not truly crystalline and contains some fluoride-ion vacancies [La80], a bond strength of 0.5130 calculated from the Zr-T r_e of $\sim 2.093 \text{ \AA}$ was used rather than the value of 0.5000 expected for an ideal crystal.

Table VI. Data for barium fluorozirconate crystals containing 8-coordinate Zr and different degrees of bridging between Zr ions. The v_s value for $\beta\text{-BaZrF}_6$ (Ba CN = 10) has been changed from 562 cm^{-1} to reflect 12-coordination of Ba.

	$v_s (\text{cm}^{-1})$	$k_T (\text{mdyne}/\text{\AA})$	s_T
$\beta\text{-BaZrF}_6$	564	3.57	0.6223
Ba_2ZrF_8	544	3.32	0.5130 (from r_e)

From the data of Table VI we can write

$$k_T^{-\frac{1}{3}} = -0.084188 \cdot \ln s_T + 0.61432, \quad (14)$$

which gives the effect of bridging on k_T for barium fluorozirconates containing 8-coordinate Zr.

Table VII. Data for barium fluorozirconate crystals with different Zr coordination numbers. The k_T value for the hypothetical $BaZrT_6$ crystal with 12-coordinate Ba was calculated previously.

	$v_s (\text{cm}^{-1})$	$k_T (\text{mdyne}/\text{\AA})$	s_T
$BaZrT_6$	(607)	(4.13)	0.6667
Ba_2ZrT_8	544	3.32	0.5130 (from r_e)

Table VII gives the following equation:

$$k_T^{-\frac{1}{3}} = -0.18283 \cdot \ln s_T + 0.54847 , \quad (15)$$

which describes the effect of changing the Zr CN. This effect is larger than that due to bridging — the slope of Eq. 15 is about twice that of Eq. 14. From Eq. 15, the ν_s frequency for the hypothetical $\text{Ba}_{1.5}\text{ZrT}_7$ crystal, which has bond strengths of $4/7 = 0.5714$, is 569 cm^{-1} .

Table VIII. Data for barium fluorozirconate crystals containing 7-coordinate Zr and different degrees of bridging between Zr ions. The ν_s value for $\beta\text{-BaZr}_2\text{F}_{10}$ (Ba CN = 11) has been changed from 590 cm^{-1} to reflect 12-coordination of Ba.

	$\nu_s (\text{cm}^{-1})$	$k_T (\text{mdyne}/\text{\AA})$	s_T
$\beta\text{-BaZr}_2\text{F}_{10}$	591	3.92	0.6969
$\text{Ba}_{1.5}\text{ZrT}_7$	(569)	(3.63)	0.5714

From Table VIII, the effect of bridging on 7-coordinate Zr units can be written in the following form:

$$k_T^{-\frac{1}{3}} = -0.084152 \cdot \ln s_T + 0.60397 . \quad (16)$$

The average of the slopes of Eqs. 14 and 16 can be used to obtain the equation describing the effect of bridging in compounds containing 6-coordinate Zr:

$$k_T^{-\frac{1}{3}} = -0.084170 \cdot \ln s_T + 0.58847 , \quad (17)$$

Obviously, the sparse amount of data available for crystalline fluorozirconates limits the accuracy of the above method. However, the qualitative trends seem to be clear: if other factors are equal, ν_s increases with decreasing countercation radius, increasing countercation CN, decreasing Zr CN, and increasing degree of bridging. Table IX is the result of attempts to quantify the separate effects of these influences and should be correct in at least the *relative* magnitudes of the frequencies shown.

D. EFFECT OF COUNTERCATION CHARGE

The charge on the countercations surrounding a given type of ZrF_n group can have a sizable effect on the symmetric stretching frequency. As an example, Li_2ZrF_6 and MgZrF_6 have the same Zr CN (6) and F-about-Zr arrangement (discrete ZrT_6^{2-} anions), the same countercation CN (6), and almost the same countercation radius (0.76 Å for Li vs. 0.72 Å for Mg). However, the ν_s for Li_2ZrF_6 is 585 cm^{-1} [To73b], and for MgZrF_6 it is 669 cm^{-1} . The size difference is very small and would account for only about 4 cm^{-1} of the difference in frequency.

Although it seems that the substitution of monovalent countercations for divalent ones serves to decrease ν_s , there apparently is no systematic way to predict directly the effects of substitution; rather, the two classes of crystals must be considered separately. A table analogous

Table IX. Estimated barium fluorozirconate frequencies in cm^{-1} for different types of ZrF_n polyhedra. Terminal and bridging (corner or edge) fluorides are denoted by T and B, respectively. Diagonal lines enclose structures with the same composition.

$\text{Zr CN} \rightarrow$	6	7	8	
a	ZrT_6 608	ZrT_7 569	ZrT_8 541	33.3 mol % ZrF_4
b	ZrT_5B 615	ZrT_6B 574	ZrT_7B 545	$F/\text{Zr} = 8.0$
c	ZrT_4B_2 622	ZrT_5B_2 579	ZrT_6B_2 550	36.4 mol % ZrF_4
d	ZrT_3B_3 630	ZrT_4B_3 585	ZrT_5B_3 554	$F/\text{Zr} = 7.5$
e		ZrT_3B_4 591	ZrT_4B_4 559	40.0 mol % ZrF_4
f		ZrT_2B_5 598	ZrT_3B_5 564	$F/\text{Zr} = 7.0$
g			ZrT_2B_6 570	44.4 mol % ZrF_4
h			ZrTB_7 576	$F/\text{Zr} = 6.5$
				50.0 mol % ZrF_4
				$F/\text{Zr} = 6.0$
				57.1 mol % ZrF_4
				$F/\text{Zr} = 5.5$
				66.7 mol % ZrF_4
				$F/\text{Zr} = 5.0$
				80.0 mol % ZrF_4
				$F/\text{Zr} = 4.5$

to Table IX can be constructed for the case of a monovalent cation. We will use 8-coordinate Na^+ and 6-coordinate Li^+ as the base counterations. The slopes of eqs. 7 and 8 are applicable to monovalent fluorozirconates, because they were derived for crystals which have similar structures and differ only in countercation size or CN. Eqs. 14-17, on the other hand, apply to crystals with the same countercation but with ZrF_n units differing in degree of bridging or in Zr CN. Therefore, Eqs. 14-17 apply specifically to 12-coordinate Ba and would be expected to have different slopes when determined for monovalent counterations.

To illustrate, the frequency for $(\text{Na}\{6\})_2\text{ZrT}_6$ (which is not known to exist) can be calculated from the $(\text{Li}\{6\})_2\text{ZrF}_6$ frequency from the following equation, which has the same slope as Eq. 6:

$$k_T^{-\frac{1}{3}} = 0.064732 \cdot r_M + 0.58962 . \quad (18)$$

This yields a frequency of 563 cm^{-1} . In order to change 6-coordinate Na ($r_M = 1.02 \text{ \AA}$) to 8-coordinate ($r_M = 1.18 \text{ \AA}$), we use an equation with the slope of Eq. 7:

$$k_T^{-\frac{1}{3}} = -0.020774 \cdot r_M + 0.67684 . \quad (19)$$

This gives 567 cm^{-1} for the 6a position of the new table. The crystal Na_3ZrF_7 contains 7-coordinate Na ($r_M = 1.12 \text{ \AA}$) and has a v_s of 556 cm^{-1} [To73b]. Its analog with 8-coordinate Na would have a frequency of 558 cm^{-1} . We can now calculate the equation analogous to Eq. 15:

$$k_T^{-\frac{1}{3}} = -0.044951 \cdot \ln s_T + 0.63410 . \quad (20)$$

As expected, the slope of the equation for Zr CN dependence is different for the cases of monovalent and divalent counterations. In fact, the slope of Eq. 20 (monovalent) is about one-fourth that of Eq. 15 (divalent). Using Eq. 20, we obtain an estimated v_s of 550 cm^{-1} for $(\text{Na}\{8\})_4\text{ZrT}_8$.

To investigate the effect of bridging, it is necessary to know the v_s for a sodium fluorozirconate with bridging fluorides. The compound $\text{Na}_7\text{Zr}_6\text{F}_{31}$ contains Na with an average CN of 10.3 and 8-coordinate Zr with 6 bridging fluorides (F/Zr ratio = 5), but there is an "extra," nonbonded fluoride for every 6 Zr ions [Bu68]. This probably serves to make the known frequency of 548 cm^{-1} artificially low. (It would be even lower when adjusted to 8-coordinate Na.) Instead, the v_s of 525 cm^{-1} for $(\text{K}\{8\})_2\text{ZrT}_4\text{E}_4$ [To73b] will be adjusted to the frequency appropriate to $(\text{Na}\{8\})_2\text{ZrT}_4\text{E}_4$ — i.e., 550 cm^{-1} . This means that, within the limitations of the very approximate framework outlined above, the effect of bridging on v_s in fluorozirconates containing monovalent counterations is negligible. This result agrees with the Raman spectra of lithium/sodium fluorothorate melts, which showed no effect on v_s as bridging increased around the 7-coordinate Th ions [To73c].

In analogy with the behavior of divalent fluorozirconates, it is probable that there is actually a small increase due to bridging in monovalent fluorozirconates. It is also expected that the effect of bridging would be more pronounced for lower Zr coordination numbers. Table ^{VII}
^X summarizes the estimated frequencies for sodium fluorozirconates.

V. DISCUSSION

A. ORIGINS OF ENVIRONMENTAL EFFECTS

1. Countercation Radius

Two things happen as the countercation radius is decreased: 1) the charge-to-radius ratio, or the field strength, of the countercation increases, and 2) the ZrF_n species are packed together more closely. The first condition would be expected to decrease the Zr-T bond strength (and ν_s) because of enhanced competition from the countercations for the terminal fluorides. The second would be expected to increase ν_s because of increased fluoride-fluoride repulsions between the more closely packed units. The overall result, an increase in ν_s , is due to the dominant force, which happens to be the packing effect. The general trend of an increase in frequency with decreasing size of countercation in infrared spectroscopy has been noted by Adams [Ref] and by Ferraro [Ref]. The same trend is observed in Raman spectra of fluorothorate melts [To73c] and fluoroberyllate crystals and melts [Ba75].

2. Countercation Coordination Number

As the countercation coordination number is increased, it is expected that the packing around the countercations would become more efficient, leading to greater fluoride-fluoride repulsions between neighboring ZrF_n units and an increase in ν_s . This is seen to be the case, but the effect is not very pronounced. The magnitude of the slope of Eq. 6 (radius) is over 3 times the magnitude of the slope of Eq. 7 (CN).

3. Zirconium Coordination Number

The CN of the central cation is known to exert a predictable and significant effect on Raman stretching frequencies [Adams]. An increase in CN always leads to a decrease in frequency due to the decrease in bond order, as seen from Tables VI and VII. The effect of changing the zirconium coordination number in fluorozirconates is larger than the effect of bridging: the slope of Eq. 15 (Zr CN) is about twice that of Eq. 14 (bridging).

4. Degree of Bridging about Zirconium

The occurrence of bridging around Zr (with the CN kept constant) leads to an increase in ν_s . It is known from fluorozirconate crystal chemistry that bridging gives rise to shorter terminal bonds [Ko82]. As Zr-T bonds are replaced by longer, weaker Zr-B bonds, electron density on the Zr is shifted to the remaining Zr-T bonds. So, even though the average bond order as defined by Eq. 10 does not change, the *terminal* bonds (which are the source of the ν_s band [Al83]) are stronger than before. In addition, the average strength of a bridging bond (assumed earlier to be a certain fraction of the terminal bond strength) increases with increased bridging. These trends were recognized by Almeida and Mackenzie [Al83], who studied fluorozirconates and fluorohafnates.

The manifestation of the decrease in Zr-T bond length in the form of ν_s requires the assumption of separability of the motions of the different types of fluorides (bridging or nonbridging) about the Zr ion. In other words, separability of fluoride-ion movements means that a normal mode of vibration can be approximated as involving primarily one type of fluoride-ion movement. Any cooperative movement between different types of fluorides would necessarily entail the movement of the zirconiums. Since a zirconium ion is about five times heavier than a fluoride ion, the Zr ions can be considered to remain motionless on the timescale of fluoride-ion movements, and the approximation of separability is acceptable in this case. Crystalline chlorocadmates (Cd/Cl weight ratio is ~ 3) show the same trend of increased terminal-ligand frequency with increased bridging [Cl72].

For lighter central cations, however, this picture is inadequate. In the case of melts containing beryllium fluoride, Toth et al. [To73a] have shown that increased bridging about Be leads to a decrease in the totally symmetric stretching frequency. Separability cannot be assumed in this case because the weight of a Be ion is about half that of a fluoride ion, and Be is therefore ineffective in behaving as a "buffer" between movements of different types of fluorides. The Raman bands are due to normal modes involving the Be_xF_y polymeric unit as a whole. The decrease in frequency is due, not to a decrease in overall bond order, but to a greater value of the reduced mass of the vibrating species.

5. Countercation Charge

The effect of the countercation charge on ν_s is related to the packing effect mentioned above. For a given F-to-Zr ratio, the number of monovalent countercations needed for charge balancing is twice the number necessary for divalent countercations. This means that, if all other factors are equal, i.e., countercation radius, countercation CN, Zr CN, and degree of bridging, then the packing requirements will be more stringent in the case of divalent countercations, and the ν_s will be higher. The extra monovalent cations provide more shielding between the ZrF_n units. Perhaps the effectiveness of monovalent countercations in separating the ZrF_n groups helps to explain the greatly lessened consequences of bridging and Zr CN on the ν_s frequencies of monovalent fluorozirconates as compared to divalent fluorozirconates.

B. APPLICATION TO INTERPRETATION OF GLASS SPECTRA

Assuming that the frequencies presented in Table IX are roughly correct, some possible structures for a fluorozirconate glass with a given composition are immediately precluded. Fig. 6 shows the Raman spectra obtained by Almeida and Mackenzie [Al81] for three binary barium fluorozirconate glass compositions. For the composition containing 64 mol % ZrF_4 (referred to as the dizirconate composition), the measured ν_s value is 580 cm^{-1} . From a comparison with the ν_s of 585 cm^{-1} of Li_2ZrF_6 , the authors concluded that the Zr ions were 6-coordinate. From the F-to-Zr ratio of the composition, they added the requirement that 2 of the 6 fluorides be bridging. This structure corresponds to the ZrT_4B_2 unit in position 6c of Table IX. However, Table IX predicts an approximate ν_s of 622 cm^{-1} for this proposed structure in the presence of 12-coordinate Ba^{2+} countercations. For the dizirconate composition, the structures possessing the frequencies closest to the experimental one are found in positions 8g and 7e — in other words, in

the columns containing 7- and 8-coordinate Zr.

It is reasonable that the ZrT_4B_2 structure proposed by Almeida and Mackenzie would have such a high frequency, since it applies to 6-coordinate Zr with divalent counterions (recall the v_s of 669 cm^{-1} for $MgZrF_6$). In addition, there is bridging in the structure, a condition which serves to increase the frequency. So even if the predicted frequency of 622 cm^{-1} is too high by a relatively large amount, even, say, 30 cm^{-1} , the v_s frequency of a barium fluorozirconate glass with ZrT_4B_2 units would still be expected to be much higher than the observed frequency of 580 cm^{-1} . Almeida and Mackenzie reject the idea of 8-coordinate Zr in the glasses on the basis of the v_s of only 525 cm^{-1} for $\alpha-K_2ZrF_6$, which is known to contain Zr in 8-coordination. But, as discussed in Section V.A., the effects of raising the counterion CN and replacing monovalent cations by divalent ones both contribute to a higher v_s . Also, since $\alpha-K_2ZrF_6$ has a F-to-Zr ratio of 6, an additional two fluorides would have to be bridging in order to satisfy the dizirconate F-to-Zr ratio of 5; this would lead to an even higher value of the expected frequency. In the end, the predicted frequency of the 8-coordinate ZrT_2B_6 unit in Table IX is 570 cm^{-1} , not too far from the observed v_s of 580 cm^{-1} .

The v_s value of 565 cm^{-1} for the 52 mol % ZrF_4 glass in Fig. 6 also coincides with the expected frequency for bridged, 8-coordinate Zr ions. Table IX predicts a value of about 559 cm^{-1} for the unit in position 8e.

The glass with 74 mol % ZrF_4 has a v_s of 598 cm^{-1} , and Table IX gives an interpolated frequency of about 573 cm^{-1} for 8-coordinate ZrF_n units. To account for the higher measured frequency, it must be assumed that 7-coordinate Zr is occurring in greater proportions for this glass composition than in the others. In fact, the interpolated frequency from Table IX for 7-coordinate Zr polyhedra at a composition of 74 mol % ZrF_4 is 595 cm^{-1} , leading to the conclusion that the main peak for this glass is due predominantly to 7-coordinate Zr units.

An interesting sideline about the utility of Table IX is its interpretation of the origin of the high-frequency shoulder at about 628 cm^{-1} in the spectrum of the 74 mol % ZrF_4 glass in Fig. 6. Almeida and Mackenzie attributed this feature to the presence of 5-coordinate Zr in the glass, even though 5-coordination of Zr has never been observed in fluorozirconate crystals. The frequency agrees with the interpolated v_s of 626 cm^{-1} for a mixture of the 6-coordinate ZrT_4B_2 and ZrT_3B_3 units of Table IX. The apparent tendency of Zr to adopt lower coordination numbers in the 74 mol % ZrF_4 glass is understandable in light of the low F/Zr of about 4.7 for this composition.

C. APPLICATION TO INTERPRETATION OF CRYSTAL SPECTRA

Another point can be made in the application of Table IX to the explanation of the v_s value (560 cm^{-1}) of the $\alpha-BaZrF_6$ crystal. In the report of the crystal structure of this polymorph [La78], it was mentioned that the ZrT_5B_2 structure of $\alpha-BaZrF_6$ is clearly more irregular than that found in $K_2Cu(ZrF_6)_2 \cdot 6H_2O$ and that the crystal can alternatively be described as containing 8-coordinate Zr units connected together in zigzag chains. In this case, Table IX predicts a frequency of 559 cm^{-1} rather than the 579 cm^{-1} expected for 7-coordination. However, the inclusion of the 8th relatively distant F from a neighboring ZrF_n group does not alter the

Table X. Estimated fluorozirconate frequencies in cm^{-1} for different types of ZrF_n polyhedra with monovalent counterions. Two frequencies immediately below a ZrF_n unit refer respectively to $\text{Na}\{8\}$ and $\text{Li}\{6\}$ ions, and a frequency in brackets is the frequency calculated for a Na/Li mole ratio of 0.535/0.465. Terminal and bridging (corner or edge) fluorides are denoted by T and B, respectively. Diagonal lines enclose structures with the same composition.

Zr CN →	5	6	7	8	
a	ZrT_5 578,596 [586]	ZrT_6 567,585 [575]	ZrT_7 558,576 [566]	ZrT_8 550,568 [558]	20.0 mol % ZrF_4
b	ZrT_4B [>586]	ZrT_5B [>575]	ZrT_6B [-566]	ZrT_7B [-558]	$\text{F/Zr} = 8.0$ 22.2 mol % ZrF_4
c		ZrT_4B_2 [>575]	ZrT_5B_2 [-566]	ZrT_6B_2 [-558]	$\text{F/Zr} = 7.5$ 25.0 mol % ZrF_4
d		ZrT_3B_3 [>575]	ZrT_4B_3 [-566]	ZrT_5B_3 [-558]	$\text{F/Zr} = 7.0$ 28.6 mol % ZrF_4
e				ZrT_4B_4 [-558]	$\text{F/Zr} = 6.5$ 33.3 mol % ZrF_4
f				ZrT_3B_5 [-558]	$\text{F/Zr} = 6.0$ 40.0 mol % ZrF_4
					$\text{F/Zr} = 5.5$

essential character of the basic ZrT_5B_2 unit and may therefore lead to a kind of "quasi- ZrT_5B_3 " structure, as viewed by Raman spectroscopy. Table IX shows a ν_s of 554 cm^{-1} for this structure (556 cm^{-1} when s_T is calculated assuming two edge bonds and one corner bond rather than 3 "bridging" bonds). This interpretation explains the otherwise-puzzling relative order of the ν_s values of β - $BaZrF_6$ (562 cm^{-1} , Ba CN of 10, Zr CN of 8) and α - $BaZrF_6$ (560 cm^{-1} , Ba CN of 11, ostensible Zr CN of 7).

D. APPLICATION TO INTERPRETATION OF MELT SPECTRA

Toth et al. [To73b] obtained Raman spectra for fluorozirconate melts containing Li and Na as countercations. They concluded that the melts contained discrete ZrF_n^{4-n} complex ions, where n is between 5 and 8 (and perhaps can be 4). Table YH1, prepared for the case of ZrF_n units in the presence of 8-coordinate Na, is applicable to the interpretation of melt spectra if it is assumed that the frequencies do not change drastically with increasing temperature (a justifiable assumption, according to Toth et al. [To73b]) and that Na is close to 8-coordinate in the melt. It will also be assumed that Li is 6-coordinate in the melt and that the ν_s values can be calculated from 0.535 times the Na value plus 0.465 times the Li value, in accordance with the mole ratios of these ions in the melts.

Toth et al. assumed the existence of 8-coordinate Zr in the melt when the F/Zr ratios were very high (between 8 and ~10). This seems to be a viable assumption, since the melt frequency from Table X for ZrF_8^{4-} is 558 cm^{-1} . As the F/Zr ratio is decreased, the ν_s values increase. This was interpreted by Toth et al. as evidence for a decrease in the average Zr CN, and this also seems reasonable. Table X predicts frequencies of 566 and 575 cm^{-1} for ZrF_7^{3-} and ZrF_6^{2-} anions, respectively.

The lowering of the F/Zr ratio below 6 seems to have caused a somewhat abrupt jump in the ν_s , as well as the appearance of a new low-frequency band at 165 cm^{-1} . For the 40 mol % ZrF_4 melt (F/Zr ratio of 5.5), Toth et al. conclude from the relatively high frequency of 593 cm^{-1} that species with 4- or 5-coordinate Zr are present. The existence of neutral ZrF_4 molecules in the melt would be a little surprising, considering the well known volatility of ZrF_4 at elevated temperatures, but 5-coordinate Zr has been indicated previously in surface-tension measurements of fluorozirconate melts containing monovalent counterions [Me64]. Table X predicts a ν_s of 586 cm^{-1} for ZrF_5^- , which is somewhat low. Although the presence of some 4-coordinate Zr cannot be ruled out, it is also possible that a higher ν_s could be due to the formation of $Zr_2F_9^-$ dimers. The existence of such dimers in fluorozirconate melts has been claimed [Ref]. It is conceivable that the occurrence of bridged 5-coordinate ZrF_n groups would lead to an extra feature in the bending region of the spectrum; this would explain the 165 cm^{-1} peak. The experimental and calculated frequencies are compared in Table XI.

Table XI. Measured Raman frequencies for $LiF-NaF-ZrF_4$ melts at a constant $LiF-NaF$ ratio of 0.465/0.535. Experimental data are taken from Ref. [To73b].

Mol % ZrF ₄	F/Zr Ratio	Measured v _s (cm ⁻¹)	Calculated v _s (cm ⁻¹)	Species Present
14	10.14	555	558	ZrF ₈ ⁴⁻
20	8.00	554	558	ZrF ₈ ⁴⁻
25	7.00	568	566	ZrF ₇ ³⁻
29	6.45	573	571	ZrF ₇ ³⁻ + ZrF ₆ ²⁻
33	6.03	577	575	ZrF ₆ ²⁻
40	5.50	593	?	ZrF ₆ ²⁻ + ZrF ₅ ⁻ + Zr ₂ F ₉ ⁻ ? + ZrF ₄ ??

It is not known to what extent these observations would be applicable to melts containing divalent counterions, but the effects of bridging, if present, would be expected to be much more noticeable in the divalent-counterion melts. The higher viscosities of the melts with divalent cations [Hu83, Sh84] may indicate an increased occurrence of bridging. It seems that further spectroscopic studies focusing on variations in composition and temperature of fluorozirconate melts would be very useful. A better understanding of the melt structure would elucidate the properties of "fragile" liquids (as described by Angell [An85]) and would probably lend insight into glass formation in these systems.

VI. CONCLUSION

The approach outlined in this paper is approximate and involves many assumptions. Even so, it appears to provide a plausible explanation for the observed v_s frequencies in binary barium fluorozirconate glasses and crystals, as well as monovalent-counterion fluorozirconate melts. If there are inaccuracies in the absolute magnitudes of the predicted frequencies for given structures, it is at least probable that the relative magnitudes are correct. In spite of the paucity of available data, there are definite, identifiable trends in the effects of certain variables on the v_s frequencies. We have attempted to analyze and quantify these trends in order to clarify the murky situation which has surrounded the interpretation of fluorozirconate glass data for some time. As an example, we quote Kawamoto [Ka83]: "...no consistent correlation can be deduced between the v_s and the F coordination number of Zr in fluorozirconate compounds.... Moreover, when bridging takes place between the F complex ions it should give many complicated effects on the v_s vibrations.... The above concludes that the Raman v_s frequency can not be utilized as a reliable guide for identifying the F coordination number of Zr in a fluorozirconate complex with unknown structure." We hope to have disproved these statements, at least to some degree.

The most important conclusion to be drawn from the above treatment is that the idea of 8-coordination of Zr in some barium fluorozirconate glasses is *not* inconsistent with the experimentally observed results from Raman spectroscopy. It must also be noted that the method can be related to bond lengths, through its connection to bond strengths (Eq. 11). This means that results from experimental methods which yield information in terms of bond lengths (such as EXAFS) should be interpreted with the same care as the frequencies from Raman spectroscopy. In other words, comparison of EXAFS fluorozirconate glass spectra with those

from alkali-metal fluorozirconate crystals is not advised and can lead to wrong conclusions, as we believe is the case in [Ma88]. In addition, only average bond lengths are obtained from EXAFS. This means that if bridging is involved, the interpretation of results becomes even more ambiguous.

The differences between the prototypical dizirconate glass spectrum and the β -BaZr₂F₁₀ spectrum lend further support to the idea that the structures of the glass and crystalline forms of this composition are different [Ph87]. The structural differences between glass and crystal are presumed to contribute to the ability of the dizirconate melt to form a glass in spite of its unfavorable ("fragile" [An85]) viscosity-temperature relation. Even though β -BaZr₂F₁₀ is formed as a major crystallization product upon heating of the glass [Pa85], its formation from the melt has been postulated to be hindered by the required arrangement of 7-coordinate Zr ions into a 2-dimensional, layered type of structure [La88,Ph87].

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